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SALT ADDITIVES EFFECTS ON THE ACTIVATION PARAMETERS OF
HETEROLYTIC REACTIONSВПЛИВ ДОБАВОК СОЛЕЙ НА АКТИВАЦІЙНІ ПАРАМЕТРИ ГЕТЕРОЛІТИЧНИХ
РЕАКЦІЙ

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Abstract. Additives of salts are powerful tools of a reaction's run. They can change the rates and stereochemistry of the reactions, alter the directions of reagents' attacks. But their effects on activation parameters of the reactions have not studied yet. In the paper the influence of salts on the rates of monomolecular heterolytic reactions under 14- 36 °C was studied, the reactions' activation parameters (ΔH^\ddagger , ΔS^\ddagger , ΔG^\ddagger) were determined both in the absence and in the presence of salt under conditions of normal salt effect. It was proved that normal salt effect in these conditions had a purely catalytic nature. The catalytic action of the salt's cation reduced reaction's ΔH^\ddagger , but such action of the salt's anion increased reaction's ΔS^\ddagger .

Key words: activation parameters, normal salt effect, catalysis, activation enthalpy, activation entropy, unimolecular heterolysis.

Introduction. The effect of salt additives on the course of reactions can be powerful and versatile. Additives of salts change the speed of reactions, affect their stereochemistry, change the direction of reagents' attacks. The most prominent are the salt effects in the reactions of unimolecular heterolysis, which run through consecutive formation of a number of polar cationic intermediates (Dvorko *et al.*, 2007).

Linear increase of the reaction rate with increasing of salt's concentration C_{salt} is called "normal salt effect" and is quantitatively described by Winstein equation (1):

$$k_s = k_0[1 + bC_{\text{salt}}], \quad (1)$$

where k_s – rate constant of the reaction in the presence of the salt with concentration C_{salt} , k_0 – rate constant of the reaction in the absence of a salt, b – salt efficiency parameter.

For a normal salt effect $b = \text{const} > 0$. The normal salt effect was explained by the increase in the ionic strength of the solution when salt was added. This explanation is refuted by experiments, since there are many cases where salts do not affect at all the rates of unimolecular heterolysis reactions, but other salts exhibit a normal salt effect under the same conditions, and different salts in solutions having the same ionic strength give different acceleration to the same reaction (salt efficiency parameter b typically varies from 4 to 40) (Dvorko *et al.*, 2007). An alternative explanation, which is also sometimes taken as such that requires no



evidence, is that the covalent substrate RX reacts with nucleophile Y to form a parallel reaction flow by S_N2 mechanism (Fig. 1).

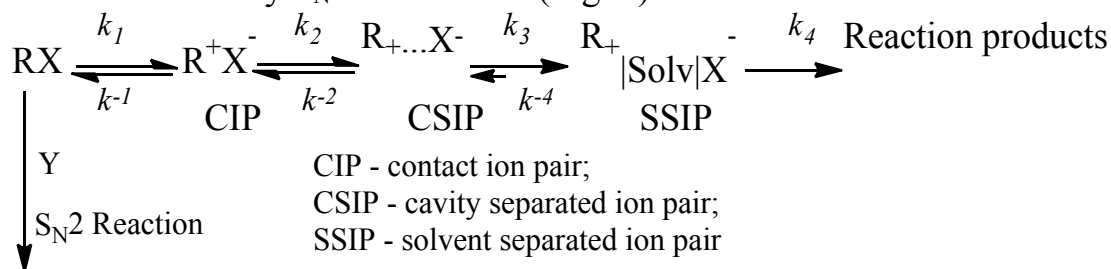


Fig 1. Scheme of unimolecular heterolysis reactions

A source: (Dvorko *et al.*, 2007)

Main Text. To advance the studies of the nature of normal salt effect, we measured kinetics of 2-chloro-2-phenylpropane (cumyl chloride) heterolysis, including runs in the presence of LiClO₄ additives (normal salt effect under the action of Li⁺ cation) and kinetics of 2-bromo-2-methylpropane (tert-butyl bromide) heterolysis in acetonitrile, including runs in the presence of Bu₄NBr additives (normal salt effect under the action of Br⁻ anion) in the temperature range 14-36 °C by Verdazyl method, elaborated by Dvorko and co-workers (Dvorko *et al.*, 2007). Activation parameters for these processes were determined both in the absence of salts as well as in their presence (Tables 1 and 2).

Table 1

Kinetic parameters of cumyl chloride heterolysis without and in the presence of lithium perchlorate additives

c(LiClO ₄)·10 ² , mol/dm ³	0	2.5	5	10
ΔH [‡] , kJ/mol	64.3 ±1.1	62.4±1.1	61.3±1.1	60.1±1.1
ΔS [‡] , J/(mol·K)	-131.1±2.3	-133.7±2.3	-134.8±2.4	-134.9±2.4
ΔG [‡] , kJ/mol	103.4±1.2	102.2±1.2	101.5±1.2	100.4±1.2

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Table 2

Kinetic parameters of tert-butyl bromide heterolysis without and in the presence of tetrabutylammonium bromide additives

c(Bu ₄ NBr)·10 ² , mol/dm ³	0	5	10	20
ΔH [‡] , kJ/mol	78.1 ±1.3	79.7 ±1.3	80.10 ±1.4	80.5 ±1.4
ΔS [‡] , J/(mol·K)	-96.3 ±2.3	-88.4±2.5	-84.9 ±2.5	-80.4 ± 2.8
ΔG [‡] , kJ/mol	106.9 ±1.4	106.0 ±1.4	105.4 ±1.3	104.5±1.3

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Our kinetic studies have confirmed the data of Dvorko and Yevtushenko, (1991) on the presence of a normal salt effect during cumyl chloride heterolysis in the presence of LiClO₄ additives and the data of Ponomareva *et al.*, (1988) on the presence of a normal salt effect on the tert-butyl bromide heterolysis in acetonitrile in the presence of Bu₄NBr additives. We extended the data of Dvorko and Yevtushenko, (1991) and of Ponomareva *et al.*, (1988) and studied each salt effect under 3 temperatures (Fig. 2 and Fig. 3 respectively) to obtain kinetic parameters of the heterolysis under presence of the corresponding salts.

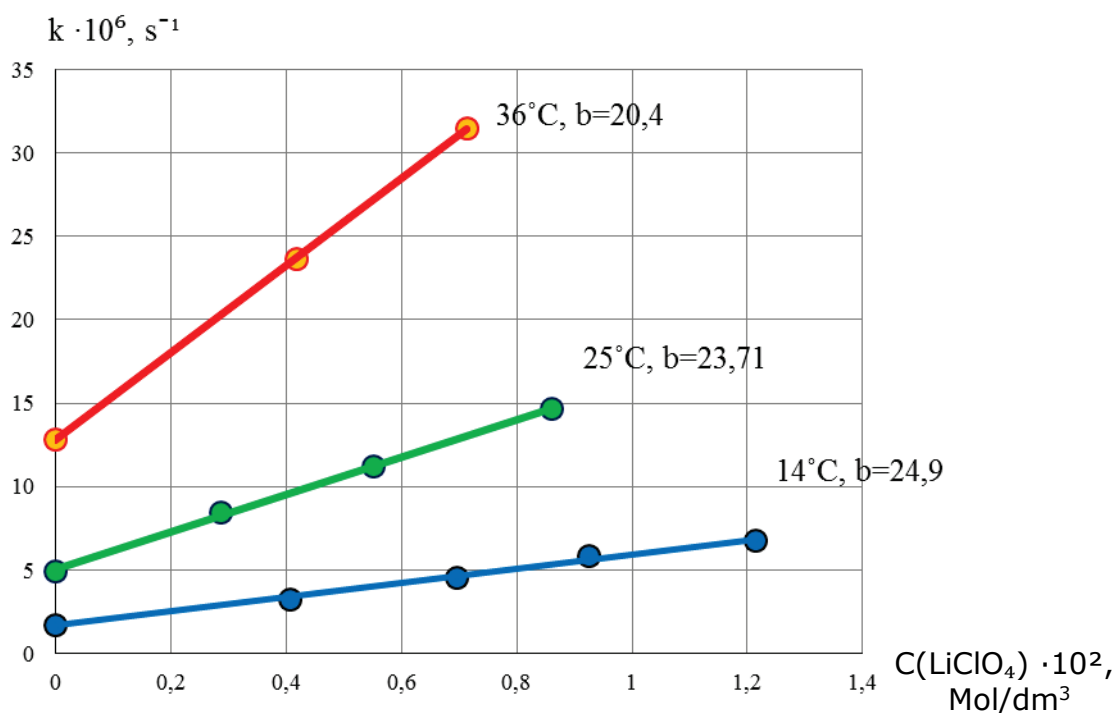


Fig. 2. The effect of the lithium perchlorate concentration on the rate of cumyl chloride heterolysis in acetonitrile under different temperatures

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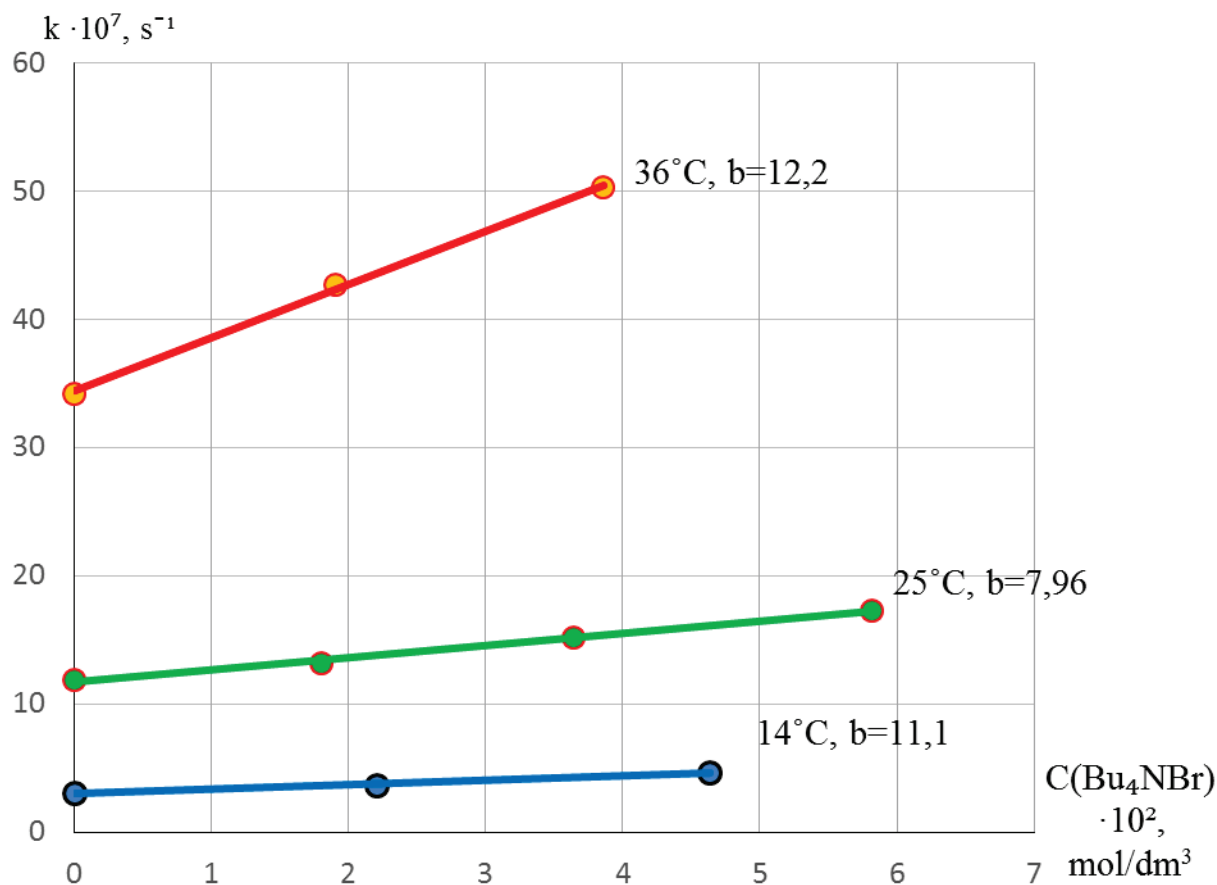


Fig. 3. The effect of the tetrabutylammonium bromide concentration on the rate of tert-butyl bromide heterolysis in acetonitrile under different temperatures

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It was found that in the presence of LiClO_4 the rate of cumyl chloride dehydrochlorination increased solely due to a decrease of activation enthalpy ΔH^\ddagger by 5 kJ/mol, while activation entropy ΔS^\ddagger remained constant (within error). Thus, for the normal salt effect caused by the action of the salt's cation, the purely catalytic nature of the salt effect was confirmed.

More complex trend has been found for t-BuBr dehydrobromination in the presence of Bu_4NBr (action of Br^- anion). In this case, free activation energy of the reaction was reduced by increase of the activation entropy ΔS^\ddagger by 16 J/(mol·K) with almost unchanged enthalpy of activation ΔH^\ddagger . Such a catalytic action is rather unusual, it can be explained by significant desolvation of reacting species under formation of the ion triplet $\text{Br}^- \cdots \text{t-Bu}^+ \cdots \text{Br}^-$ in the transition state of the reaction.

Summary and conclusions.

Temperature dependencies of cumyl chloride and t-BuBr heterolyses rates were studied by Verdazyl method in acetonitrile in the presence of salts. In all the cases normal salt effect has place. Activation parameters of heterolyses were calculated for processes in the presence of salt and without the latter.

Normal salt effect in the reactions of unimolecular heterolysis is caused by the catalytic action of the salt particles, but not by $\text{S}_{\text{N}}2$ reaction and certainly not by the increase in the ionic strength of the solution.

Catalytic action of the salt's cation reduces reaction's activation enthalpy ΔH^\ddagger , but such action of the salt's anion increases reaction's activation entropy ΔS^\ddagger .

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Анотація. Сольові ефекти потужно впливають на перебіг реакцій. Вони змінюють швидкість і стереохімію процесів, напрямок атаки реагентів. Проте вплив солей на активаційні параметри реакцій ще систематично не досліджувався. В даній статті досліджено вплив солей на швидкість мономолекулярних гетеролітичних реакцій у температурному інтервалі 14 – 36 °С, визначено активаційні параметри реакцій (ΔH^\ddagger , ΔS^\ddagger , ΔG^\ddagger) як у відсутності солей, так і у присутності солі в умовах нормального сольового ефекту. Доведено, що нормальний сольовий ефект у даних умовах має суто каталітичну природу. Каталітична дія катіону солі зменшує ентальпію активації, каталітична дія аніону солі збільшує ентропію активації реакції.

Ключові слова: активаційні параметри, нормальний сольовий ефект, каталіз, ентальпія активації, ентропія активації, мономолекулярний гетероліз.

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